Stereochemistry Lecture 1

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Stereochemistry

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Isomerism

Structural isomerism, or constitutional isomerism

Stereoisomers

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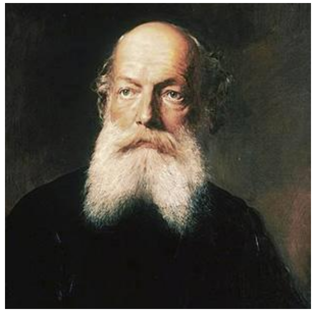
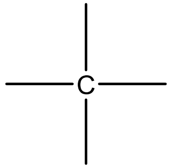
Introduction

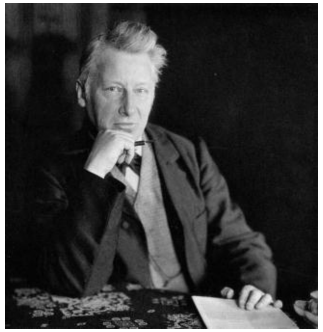


August Kekule
German Chemist

1857

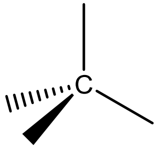


carbon is tetravalent



Van’t Hoff
the first Nobel laureate in chemistry

1874



tetrahedral arrangement of the valence bonds of carbon

Joseph Achille Le Bel.

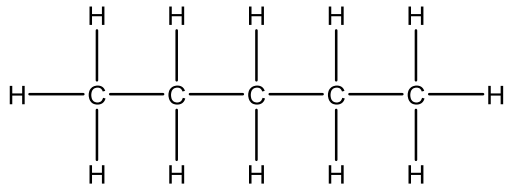
Formulas of Organic compounds

1- Molecular Formula C_5H_{12}

Not very useful for organic compounds because

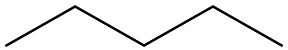
So many isomers can exist

2- Structural Formulas



3- Condensed Structural Formula $CH_3\text{-}(CH_2)_3\text{-}CH_3$

4- Bond-line Formula



- **- end of line segment represents carbon**
- **- it is assumed to satisfy each carbon's octet**

Isomerism

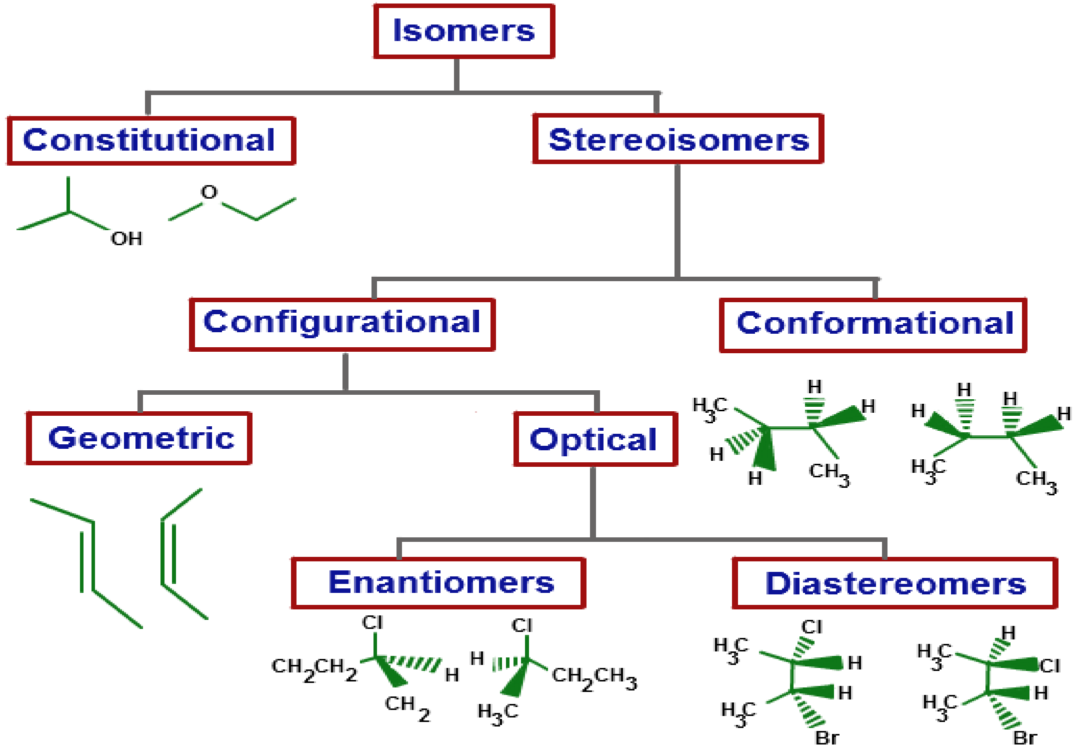
There are three major types of isomerism:

- constitutional isomerism
- Stereoisomerism
  - conformational isomerism
  - configurational isomerism
    - geometrical isomerism
    - optical isomerism
      - Enantiomers
      - Diastereoisomers

} stereoisomerism

Isomerism

Isomers have identical composition but different structures

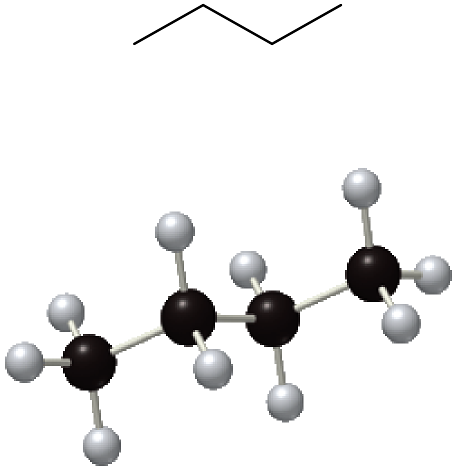


Structural isomerism, or constitutional isomerism

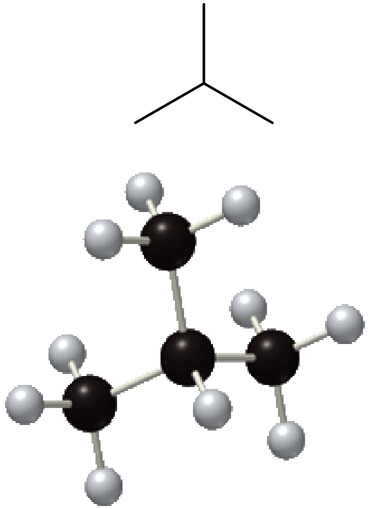
Structural isomerism, or **constitutional isomerism** (per IUPAC), is a form of **isomerism** in which molecules with the same molecular formula have different bonding patterns and atomic organization.

Eample :

- **C_4H_{10}**



Butane

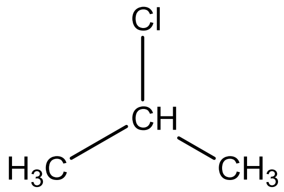


2-methyl propane

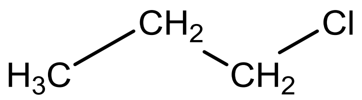
Structural isomerism, or constitutional isomerism

Eample : Different position of functional groups

- **C_3H_7Cl**

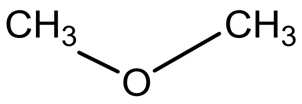


2-Chloropropane

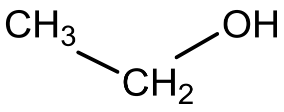


1-Chloropropane

Eample : Different position of functional groups: **C_2H_6O**



Dimethyl ether



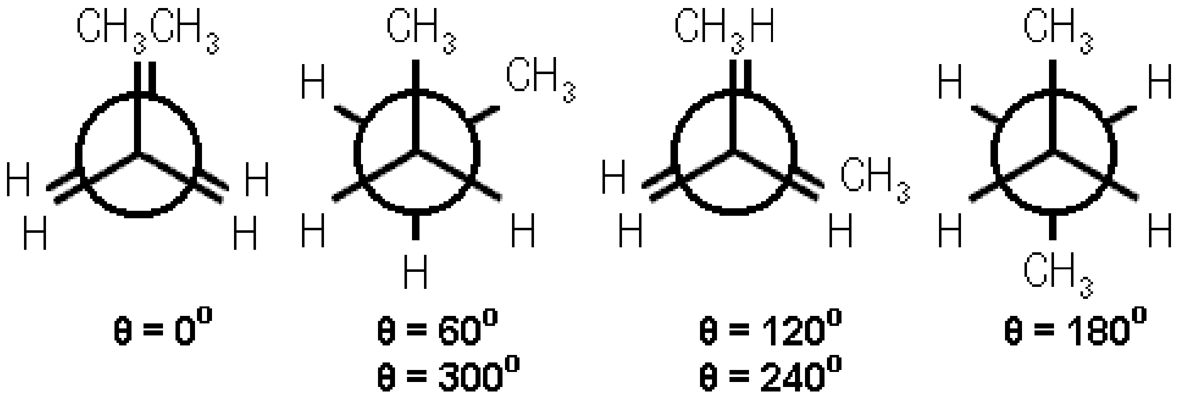
Ethanol

Stereoisomers

Stereoisomers have the same atomic connectivity but differ in the spatial arrangement of the constituent atoms.

1. **Conformational** isomers (or **conformers** or **rotational isomers** or **rotamers**) are stereoisomers produced by rotation (twisting) about σ bonds, and are often rapidly interconverting at room temperature.

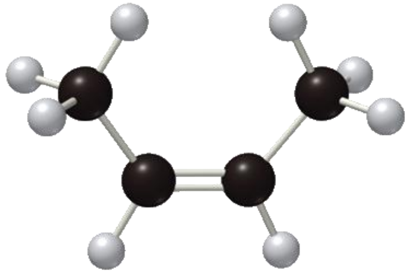
example : butane : anti (*left*) and syn (*center*). Try rotating the model to look along the C2-C3 to see the two extreme forms.



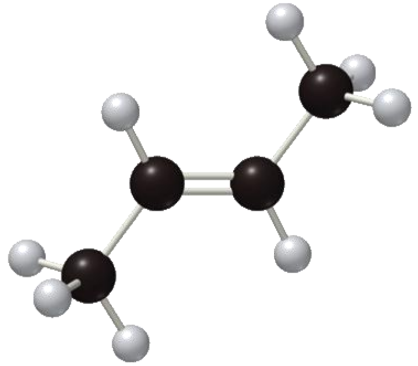
Stereoisomers

configurational isomerism:

1- geometrical isomerism: *Cis-trans* isomers have different physical and chemical properties.

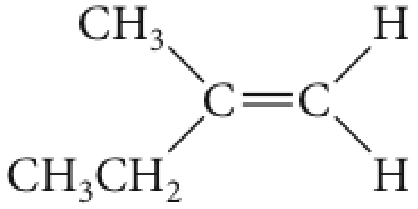


Cis-2-butene



trans-2-butene

You should be able to identify *cis-trans* isomers of alkenes when each carbon of the double bond has one substituent and one hydrogen.



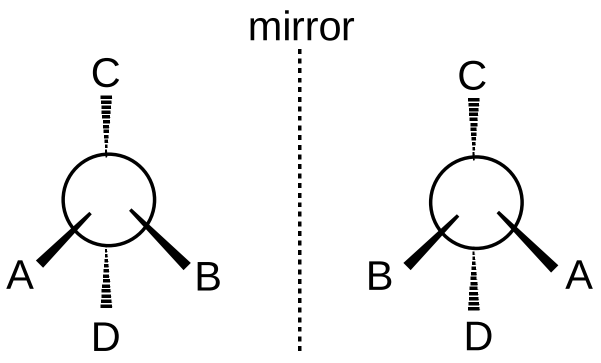
2-methyl-1-butene
(no *cis*, *trans* isomers)

Stereoisomers

configurational isomerism:

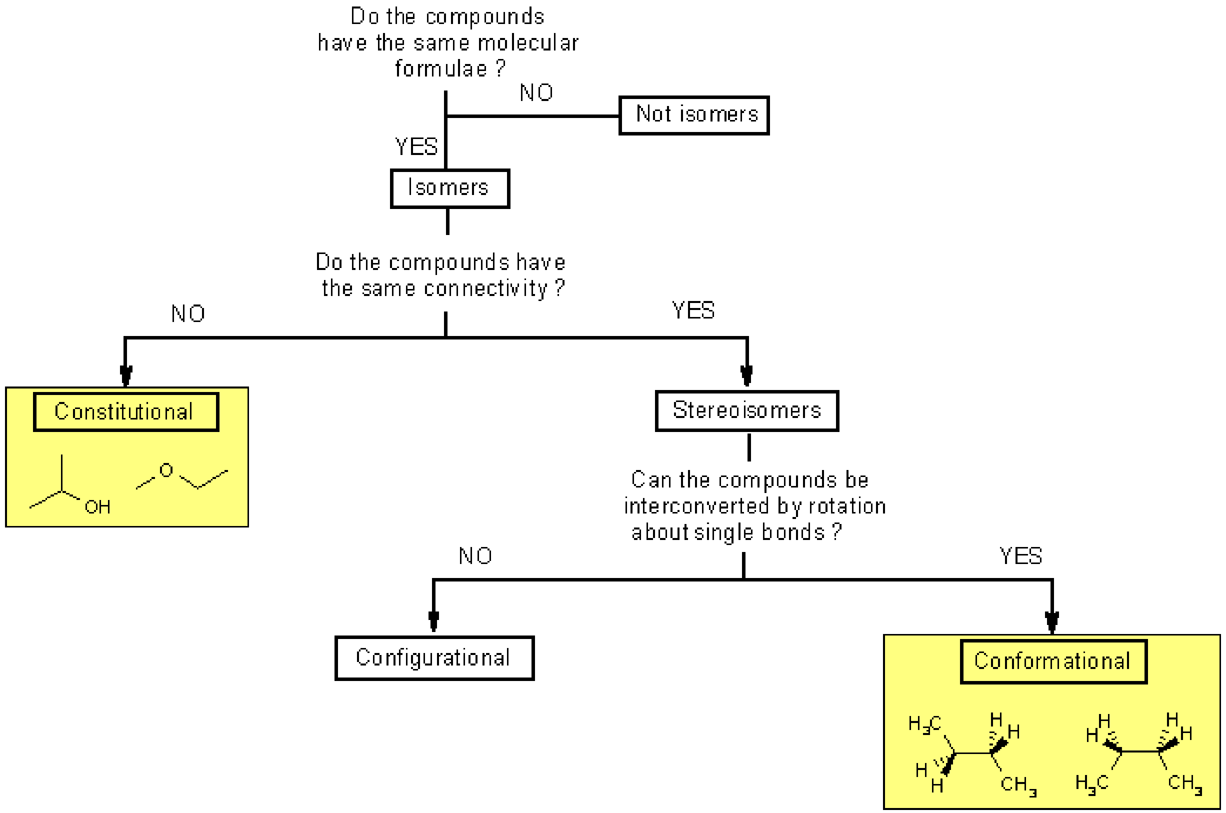
2- optical isomerism

Optical isomers are molecules that differ three-dimensionally by the placement of substituents around one or more atoms in a molecule. **Optical isomers** were given their name because they were first able to be distinguished by how they rotated plane-polarized light.



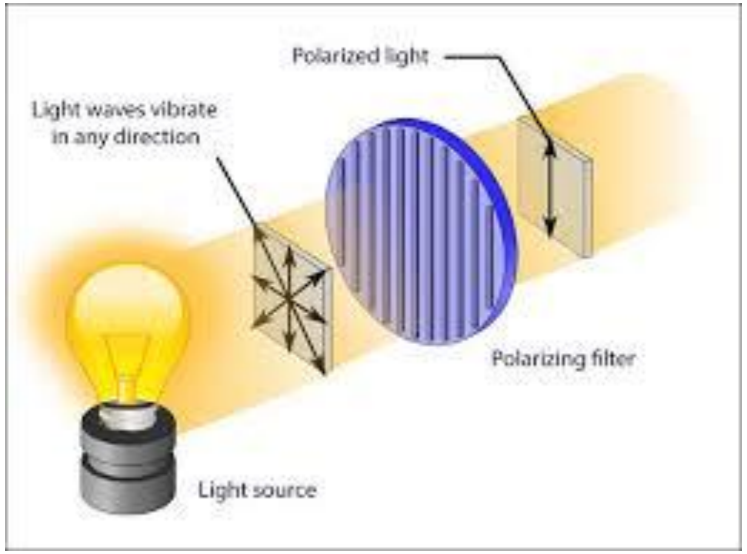
optical isomers

Stereoisomers

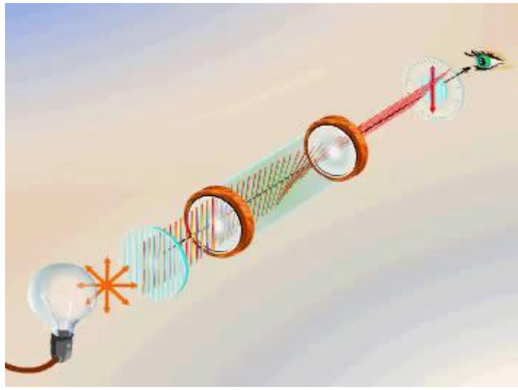


Polarized light

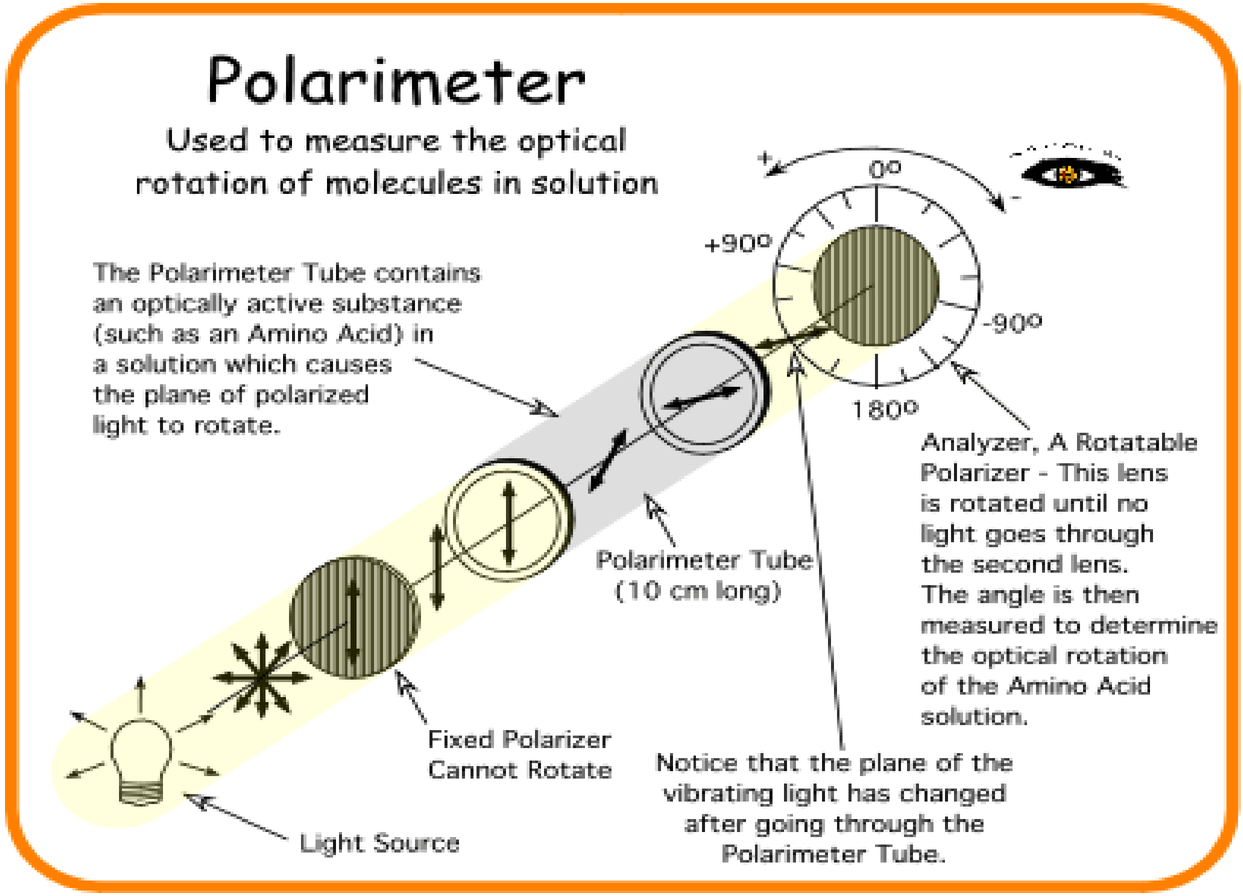
Plane polarised light is a term used to describe the polarisation state of the source **light** used in polarising microscopes. **Polarised light** is **light** that vibrates in a single direction due to its passage through a polariser.



Polarimeter



Polarimeter



Optically active compounds

An optically active compound is one which rotates the plane of polarization.

If from the vantage point of the observer the rotation is in the clockwise direction, the sample is said to be dextrorotatory. The angle of rotation, α, is considered to be positive (+).

If the rotation is in the counterclockwise direction, the sample is said to be levorotatory and the angle, α, is then negative (-).

Older terms for positive and negative rotations were *dextrorotatory* and *levorotatory*, from the Latin prefixes *dextro-* ("to the right") and *levo-* ("to the left"), respectively.

Specific rotation

α is proportional to the concentration of the sample and the length of the sample tube:

$$[\alpha]_{\lambda}^{t} = \frac{\alpha}{l \times c}$$

α - angle of rotation measured in degrees

t - temperature

λ - wavelength of light (The wavelength used most often is 589 nm (called the D line)

l - length of sample cell (in decimeters)

c - concentration in grams of substance contained in 1 mL of solution

Specific rotation

- [α] depends on the temperature and the wavelength of the light used
- these quantities are also incorporated while reporting [α]

$$[\alpha]_D^{25} = +3.12^o$$

- means D line of a sodium lamp (λ=589.6nm) is used for the light at a temperature of 25^{o}C, and that a sample containing 1.00g/ml of the optically active substance, in a 1-dm tube, produces a rotation of 3.12^o in a clockwise direction

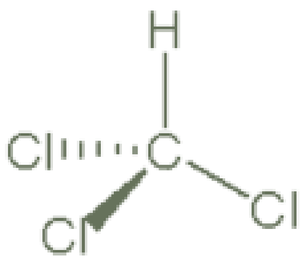
Wedge and dash Projection

- A wedge and dash projection (wedge-and-dash) is a means of representing a molecule(a drawing) in which three types of lines are used in order to represent the three-dimensional structure:

(1) solid lines to represent bonds that are in the plane of the paper,

(2) dashed lines to represent bonds that extend away from the viewer, and

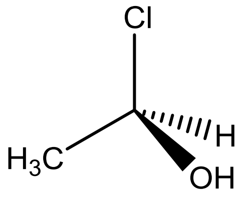
(3) wedge-shaped lines to represent bonds oriented facing the viewer.



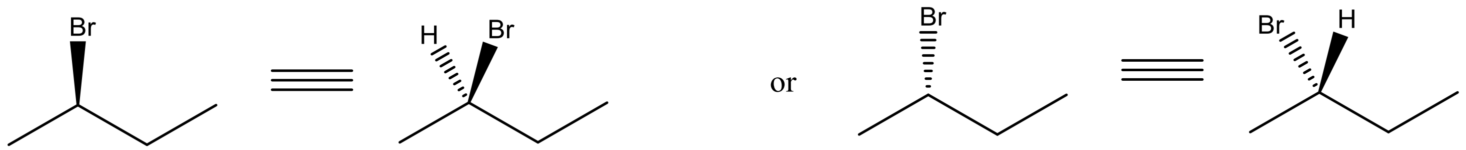
Wedge and dash Projection

- Example: Draw the wedge-dash structures for:

1. $CH_3CHClOH$



2. 2-bromobutane



Wedge and dash Projection

- Example: Draw the wedge-dash structures for:

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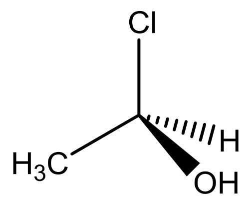

2. 2-bromobutane